

Influence of Natural Organic Matter (NOM) on Callovo-Oxfordian Clay Stability in High pH Solutions at 60°C: C(1s) NEXAFS Studies)

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Beamline(s): X1A

Introduction: High pH solutions (12.5-13.6) are typical for in the initial stage of cement alteration (1), which will occur at the engineered- geoengineered barrier boundary in a deep geological nuclear waste repository site. Although a number of publications exist on size and shape analysis of natural clay colloids (2) and the effect of high saline and high pH solutions on the clay stability (3,4), spectro-microscopic studies on natural organic matter (NOM)-clay association in high pH solutions are rare (5,6). In the present study the clay-rich formation "Callovo-Oxfordian argillite", which will be the host rock formation for the French underground laboratory was chosen to investigate the influence of a high pH plume on the clay mineralogy and chemical properties. Contrary to previous studies in pure clay systems (7), X-ray diffraction pattern showed no significant appearance or disappearance of new diffraction peaks after one-year reaction in alkaline solutions (pH 13.2) indicating a retardation of clay transformation in clay-NOM associations. To reveal details on this clay-organic interaction in the unaltered system and to elucidate the process of reaction inhibition X-ray absorption wet-cell experiments were carried out. Soft X-ray absorption spectro-microscopy at the carbon K-edge and potassium L-edge were used to visualize preferred sorption sites of NOM on the clay and to characterize the chemical composition of NOM as well as colloidal organic material released into the reaction water.

Methods and Materials: Suspension samples of Callovo-Oxfordian clay contacted with solid young fluid (SYF) (8) over a period of one day to 2 years (liquid/solid ratio of 20 and 80) as well as reaction waters (DOC concentration increase from 1.1 to 270 mg/L) were analyzed by C(1s) NEXAFS measurement. SYF solution represents the initial Ca-Na-K rich composition of cement alteration. All NEXAFS spectra were collected using a wet cell assembly (9) to prevent dehydration artifacts.

Results: The results show a complete coating of the unaltered clay by NOM with preferential sorption onto clay edges. NOM coverage of the clay basal surfaces decreased significantly with reaction time, whereas organic bonding to clay edges is still effective. The C(1s) absorption edge of the untreated NOM perceived features of aromatic carbon, carboxylic groups, aromatic carbon bonded to oxygen (e.g. phenol). The reacted samples showed equivalent features with comparable intensities of aromatic carbon and carboxylic acids, but a considerable decrease of the C(1s) continuum step in the potassium L₃-edge normalized spectra (5). Analysis of the reaction solution showed not only a clay surface release of organic matter and a decrease of the average DOC colloid size, but also a continuous increase of oxygen containing functional groups in the C(1s) NEXAFS spectra.

Conclusions: The Soft X-ray spectromicroscopy results indicate that bonding of organic ligands to clay crystal edges under oxidizing conditions plays a crucial role in the reaction kinetics of the Callovo-Oxfordian clay (future French underground laboratory). Furthermore the DOC increase with reacting time does not promote clay mineral dissolution by complexing Al and Si.

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